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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
APPLICATION FOR PATENT

5 **OPTICAL COATINGS AND ASSOCIATED METHODS**

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BACKGROUND OF THE INVENTION

 An optical coating, typically consisting of one or more layers of material, is often applied to a substrate to modify the performance of the substrate. Performance, such as the aesthetics and appearance of a substrate or the heating, cooling, and the internal daylight balance of a substrate, can be modified by coating the surface of the substrate with an optical coating. For example, an optical coating may be used to reduce the transmission of visible light (a solar control coating), decrease absorption of energy (a low-emissivity coating), or reduce reflectance (an anti-reflective coating). In addition, a substrate coated with an optical coating may need to be further modified, such as by shaping a flat substrate, to increase its commercial value. An optical coating on a substrate can be applied either before or after modification. If the optical coating is applied before modification, then the coating needs to be able to withstand the processing conditions of the modification.

 Many substrate modifications require the processing of the substrate at high temperatures. One such modification is the bending of the substrate. For example, glass can be shaped by heating it to a high temperature and then bending it. Shaped glass is important in products such as automobile windshields, side and back windows, headlights, and architectural glass. For most architectural and automotive glass, the glass typically needs to be heated above its bending temperature around 650°C in order to bend it. The temperature of a substrate is raised in other modifications, such as the heat-strengthening, the tempering, or the fritting of that substrate. For example, glass may be heat-strengthened at approximately 600°C or tempered at a temperature of approximately 730°C by blowing air on the glass after it has been bent. Heat-strengthening and tempering help substrates resist the thermal stresses caused by the absorption of heat. Tempering creates a stress field, which causes the glass to shatter into tiny pieces when

broken or cut so that people are not injured by knife-like pieces. Another example of heat treatment is the frit sealing of a substrate, such as a cathode ray tube ("CRT"), which involves heating the coated substrate to approximately 400°C.

5 Currently, an optical coating is typically deposited after the heat treatment of a substrate because the optical coating decomposes at the high temperatures used in the heat treatment of a substrate. Coating after heat treatment has some disadvantages. For example, in the coating of curved glass, coating for different sizes and shapes of the glass panes may require adjusting processing parameters and may require new tools or carriers to hold the curved glass while coating it. Such adjustments increase the cycle time and
10 thus, decrease production throughput and increase cost. Such adjustments also have an adverse effect on coating uniformity.

 It is desirable to coat a substrate before heat treatment of the substrate to avoid the disadvantages of coating after heat treatment. The process of coating first and heating later has many advantages, such as improved coating uniformity and cost efficiency from
15 economies of scale. For example, when glass is coated first and heated later, larger pieces of flat glass can be coated. Coating larger pieces of glass reduces the cost of production due to economies of scale and increases glass throughput. Another advantage is that the customer can customize the final product by cutting the coated, flat glass to size and heat treating the coated, flat glass on site. Yet a further advantage is that
20 multiple flat substrates can be coated using the same process, which is preferably optimized to provide uniform coatings. Curved substrates generally cannot be coated using the same process, as adjustments are necessary to accommodate for shape or curvature variations.

 Despite the advantages of coating first and heating later, this process is not the
25 norm in the industry. Others have reported problems with the process of coating first and heating later. Szczyrbowski et al., "Bendable Silver-Based Low Emissivity Coating on Glass," Solar Energy 19 (1989) 43-53, state that existing multi-layer coatings deposited on a transparent substrate do not withstand the heat treatment of the transparent substrate. According to the authors, a multi-layer coating on glass is destroyed at temperatures
30 higher than 350°C because a silver layer in the coating deteriorates at 250°C, as the silver agglomerates and diffuses into the oxide layers of the coating. Szczyrbowski et al. protect the silver layer by using stabilizer layers.

Another reason why stacked coatings do not survive heat treatment is that any layer, such as the top dielectric layer, may crystallize before the process reaches the high temperatures used in the heat treatment of a substrate. For example, a multi-layer stack with amorphous titanium oxide (α -TiO_x) as the top layer does not survive heat treatment to 650°C because the top layer crystallizes around 300°C. The crystallization not only forms grain boundaries, which enhance diffusion, but also causes the film to change size and partially delaminate.

SUMMARY OF THE INVENTION

10 The present invention, briefly and generally, involves an optical coating for a substrate and a method of manufacturing a coated substrate. The optical coating comprises an amorphous material, which includes titanium oxide and one or more additives. Titanium oxide and the additive in an oxidized state do not form a solid solution. Since the compounds in the amorphous layer do not form a solid solution, the amorphous layer does not change significantly and remains largely amorphous at the high temperatures used in the heat treatment of a substrate.

The amorphous film has a high refractive index and a high crystallization temperature. The type of additive in the film, index of refraction of the film, and the crystallization temperature of the amorphous film can be selected to suit the needs of a particular application of the optical coating. The amorphous film of the present invention does not significantly change its size at high temperatures, so it can help reduce or prevent oxidation of an underlying layer or stop migration of contaminants. Since the amorphous film remains largely amorphous at high temperatures, the optical properties of the stack do not change significantly after heat treatment, and the optical coating does not decompose at the high temperatures used in the heat treatment of a substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other features and aspects of the present invention will become more apparent upon reading the following detailed description in conjunction with the accompanying drawings, in which:

Figures 1a, 1b, 1c, and 1d are cross-sectional views of a multi-layer stack, including an amorphous film, on an underlying substrate;

Figures 2a and 2b are schematic diagrams of a sputtering process used to deposit the amorphous film on a substrate;

Fig. 3 is a graph showing the correlation between the deposition rate of the amorphous film and the temperature of the substrate;

5 Figure 4a is a graph showing the correlation between the index of refraction of the amorphous film at 550 nanometers and the crystallization temperature; and

Figure 4b is a graph showing the correlation between the approximate atomic percentage of an additive and the crystallization temperature of the amorphous film.

In the drawings, like reference symbols are used for like or similar parts.

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Detailed Description

According to the invention, an amorphous film with a high index of refraction is used for a heat treatable optical coating. The amorphous film comprises a dielectric, such as titanium oxide, and at least one additive that raises the crystallization temperature of the dielectric. The dielectric is preferably titanium oxide, since the index of refraction of titanium oxide is high in the visible range, namely 2.45 at 550 nanometers. The additive is selected such that the dielectric and the additive in their reacted states are insoluble in each other and, thus, do not form a solid solution. Since the compounds in the amorphous film do not form a solid solution, the amorphous film does not change significantly and remains largely amorphous at the high temperatures used in the heat treatment of a substrate. The additive, represented by X, is one or more of the elements of silicon, aluminum, bismuth, gadolinium, tantalum, zinc, and any other additive that is insoluble in the dielectric when the additive and dielectric are in their reacted states.

The amorphous film is advantageous in any layer of a multi-layer, heat treatable coating. The amorphous film does not change significantly its size or its optical properties, such as its index of refraction, at high temperatures. Change in the size of a layer can cause stress-related failure, such as delamination, while a change in the optical properties of a layer can alter the intended design of a coating. When the amorphous film is on top of a metal layer or a non-oxide layer, the amorphous film can reduce or prevent oxidation of the underlying layer from the atmosphere. When the amorphous film is deposited directly on the substrate, the amorphous film can reduce or prevent haze by slowing the migration of contaminants, such as sodium, in the substrate to any overlying

layers. Since the amorphous film has few, if any, grain boundaries, it has a low diffusion coefficient, so diffusion of contaminants across the film is very slow. The amorphous film can also reduce or prevent interdiffusion between the two layers surrounding it.

Appropriate additives can be selected for the amorphous film. Different methods may be used to select appropriate additives. In one method, the additives were selected by determining which elements in their oxidized states were insoluble in titanium oxide over a desired temperature range. A phase diagram was used in this determination. The horizontal axis of the phase diagram reflected the amount of titanium oxide from 0 to 100% atomic weight in a compound comprising titanium oxide and the additive in its oxidized state, while the vertical axis reflected temperature. The phase diagram was examined for a eutectic line, indicating the melting point of the solution. If no lines were present between the eutectic line and the bottom horizontal line, which represented a low temperature, then it was determined that the titanium oxide and the oxidized additive did not form a solid solution between the temperature associated with the bottom horizontal line and the temperature associated with the eutectic line. Thus, the composition of an amorphous film of titanium oxide and the oxidized additive would not change significantly between the temperature associated with the bottom horizontal line and the temperature associated with the eutectic line. If only a vertical line was present, then it was determined that the titanium oxide and the oxidized additive formed a solid solution of only one composition between the temperature associated with the bottom horizontal line and the temperature associated with the eutectic line. The composition of the amorphous film would change to that solid solution composition in that temperature range and to either a titanium oxide phase or an oxidized additive phase, depending on the percentage of the additive. However, if any other line besides a vertical line was present, then it was determined that a range of solid solutions existed at different temperatures between the temperature associated with the bottom horizontal line and the temperature associated with the eutectic line. Thus, as the temperature of the amorphous film increased, the composition of the amorphous film would become a different composition at different temperatures.

Silicon dioxide, aluminum oxide, bismuth oxide, gadolinium oxide, tantalum oxide, and zinc oxide were found to be insoluble in titanium oxide in the solid state and

thus were deemed appropriate for this invention. Other appropriate additives can be selected in the above-described manner.

5 The amorphous film has a high crystallization temperature (i.e., greater than about 300°C) and a high index of refraction (i.e., greater than about 2.1). The crystallization temperature and the index of refraction can be selected for different applications by changing the type of additive in the film and the doping level of the additive. Selecting a higher crystallization temperature results in a lower index of refraction. Conversely, selecting a higher index of refraction results in a lower crystallization temperature.

10 The crystallization temperature of the amorphous film is selected to be above the heat-treatment temperature, the temperature used in the heat treatment of a substrate, such as the bending of glass at about 650°C, heat strengthening at about 600°C, tempering at about 730°C, and fritting at about 400°C. Thus, the amorphous film will remain substantially amorphous at the heat-treatment temperature of a substrate.

15 The index of refraction of the doped dielectric layer can be selected. For example, aluminum oxide has a refractive index of about 1.7, zinc oxide and tantalum oxide have refractive indices of about 2.0, and bismuth oxide has a refractive index of about 1.9, while silicon dioxide has a refractive index of about 1.5. Some applications may require a higher index of refraction than that of the amorphous film with silicon as an additive. Thus, for amorphous films that require a higher index of refraction, aluminum, zinc, 20 tantalum, or bismuth, instead of silicon, can be used as the additive to raise the index of refraction of the amorphous film.

25 The amorphous film is particularly desirable in low-emissivity coatings and anti-reflective coatings. In a low-emissivity coating, the coating transmits visible light with low absorption and high reflection in a designated region of the solar spectrum, such as low absorption in the visible region and high reflectivity in the infrared region. A metallic layer, such as silver, reflects light in the infrared region, but also reflects light in the visible region. A thick layer of a metallic layer, such as silver, is more effective at reflecting light in the infrared region, but may cause an unacceptable increase in visible reflection, such as greater than ten percent. Visible transmission can be increased by 30 depositing layers of a material with a high-refractive index, such as a refractive index greater than about 2.1, around the metallic layer. A higher refractive index material, such as a material with a refractive index greater than about 2.1, de-reflects the visible

reflection caused by the silver better than a lower refractive index material, such as a material with a refractive index less than about 2.1, does. Thus, more silver can be used in a low-emissivity coating when a material with a higher index of refraction is used. Other materials, such as materials without an additive, that remain amorphous to elevated temperatures, do not have a high index of refraction. For example, silicon nitride remains amorphous at 1000°C for up to fifteen minutes, but only has an index of refraction of 2.0. Thus, silicon nitride is less desirable for use in a low-emissivity coating because it has a lower refractive index.

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An embodiment of a multi-layer stack with the amorphous film is shown in Figure 1a. A substrate 11, in this example, glass, is coated with a multi-layer optical coating 20. The invention comprises a coating for any substrate 11, such as a transparent substrate like a CRT or glass. The coating is particularly useful for a substrate that undergoes heat treatment, although it is generally useful for coating any substrate. A first anti-reflection layer of dielectric 13, such as titanium oxide, tin oxide, zinc oxide, or silicon nitride, is deposited over the substrate 11. The first anti-reflection layer 13 in combination with subsequent layers reduces the reflectance of visible light. In one embodiment, the first anti-reflection layer 13 may be composed of the amorphous film. A first metallic layer 17, such as silver, is deposited over the first anti-reflection layer 13. The first metallic layer 17 reflects infrared light and lowers emissivity. A second anti-reflection layer of dielectric 21, such as titanium oxide, tin oxide, zinc oxide, or silicon nitride, is deposited over the first metallic layer. The second anti-reflection layer 21 de-reflects the metallic layer by reducing the reflectance of visible light. In one embodiment, the second anti-reflection layer 21 may be composed of the amorphous film. At least one of the first anti-reflection layer 13 and the second anti-reflection layer 21 includes the amorphous film. The dielectric layers, such as the second anti-reflection 21, in the multi-layer coating may be doped with one or more additives, while other dielectric layers may be undoped. It is understood that other layers may be deposited on top of, on the bottom of, or between the aforementioned layers.

Another embodiment of the present invention is shown in Fig. 1b. A multi-layer optical coating 22 includes a first anti-reflection layer 13, a first metallic layer 17, and a second anti-reflection layer 21. One or more optional barrier layers 15 and 19 may be present on top of or below the first metallic layer 17, respectively. A first barrier layer

15, such as titanium, nickel-chromium, aluminum, or zinc, may be deposited on top of the first anti-reflection layer 13 and below the first metallic layer 17. The first barrier layer 15 reduces or prevents the diffusion of contaminants into upper layers. A second barrier layer 19, such as titanium, nickel-chromium, aluminum, or zinc, may be deposited on top of the first metallic layer 17 and below the second anti-reflection layer 21. The second barrier layer 19 reduces or prevents the diffusion of atmospheric gas, reduces or prevents the oxidation of the underlying metallic layer, and helps adhesion. The barrier layers 15, 19 may be any material that protects the first metallic layer 17 from oxidation and does not alloy with or degrade the properties of the first metallic layer 17. The barrier layers 15, 19 may promote adhesion.

Another embodiment of the present invention is shown in Fig. 1c. A multi-layer optical coating 26 includes multi-layer optical coating 22. The multi-layer optical coating 26 has a second metallic layer 35, such as silver, over the second anti-reflection layer 21, and a third anti-reflection layer of dielectric 39, such as titanium oxide, tin oxide, zinc oxide, or silicon nitride, over the second metallic layer 35. The third anti-reflection layer of dielectric 39 may comprise the amorphous film. The multi-layer optical coating may have a third barrier layer 33, such as titanium, nickel-chromium, aluminum, or zinc, between the second anti-reflection layer 21 and the second metallic layer 35, and a fourth barrier layer 37, such as titanium, nickel-chromium, aluminum, or zinc, between the second metallic layer 35 and the third anti-reflection layer of dielectric 39. At least one of the first anti-reflection layer 13, the second anti-reflection layer 21, and the third anti-reflection layer 39 includes the amorphous film.

Another embodiment of a multi-layer stack with the amorphous film is shown in Figure 1d. Fig. 1d illustrates a conventional anti-reflective coating. A substrate 11, in this example glass, is coated with a multi-layer optical coating 24. The invention comprises a coating for any substrate 11, such as a transparent substrate like a CRT or glass. While the coating is particularly useful when applied to a substrate undergoing heat treatment, it may generally be applied to any substrate. A first high-refractive index layer 12 with a refractive index greater than about 2.1 is deposited over the substrate 11. The first high-refractive index layer 12 may comprise the amorphous film. The amorphous film of the present invention can reduce or prevent haze by slowing the migration of contaminants from the substrate 11, such as sodium, from migrating to any

upper layers. Amorphous films have low diffusion coefficients because they have no grain boundaries. A first low-refractive index layer 14 with a refractive index less than about 2.1, for example, silicon dioxide or a metallic layer such as silver, is deposited over the first high-refractive index layer 12. A second high-refractive index layer 16 with a refractive index greater than about 2.1 is deposited over the first low-refractive index layer 14. The second high-refractive index layer 16 may comprise the amorphous film. A second low-refractive index layer 18 with a refractive index less than about 2.1, for example, silicon dioxide, is deposited over the second high-refractive index layer 16. At least one of the first high-refractive index layer 12 and the second high-refractive index layer 16 includes the amorphous film. The amorphous film of the present invention reduces or prevents any layer, such as an underlying layer, oxidation at the heat-treatment temperature of the substrate, such as above about 300°C. Since the amorphous film remains substantially amorphous at high temperatures, the optical properties of the stack do not change significantly after heat treatment. It is understood that other layers may be deposited on top of, on the bottom of, or between the aforementioned layers.

The deposition of any of the optical coatings 20, 22, 24, or 26 may occur by sputtering. Figure 2a is a schematic illustration of a conventional sputtering process. A cylindrical rotating target 23 comprises an outer layer composed of a material 25 to be deposited on a substrate 31. A plasma 27 is formed from gas introduced into a vacuum system. Typical gases include oxygen, nitrogen, noble gases, and other gases known in the art. Energized ions 29 in the plasma 27 are accelerated onto a target 23. The ions provide energy for atoms of the material 25 to leave the target 23 and be deposited onto the substrate 31. The sputtering may be performed by a conventional reactive sputtering process, in which the reactive ions combine with the sputtering material either at the target, the substrate, or in the plasma.

The deposition of the amorphous film may be accomplished by using a conventional doped target or by using a conventional co-sputtering process in an oxygen environment. The doped target comprises a metallic material doped with the additive. Co-sputtering involves the use of two targets, as shown in Fig. 2b, one coated with the metallic material 35 and the other with the additive 33.

The deposition of the amorphous material occurs under conditions in which the film has an amorphous (glassy) structure, called a-TiXO. The additive, in the oxidized

state, represented by XO_x , is largely insoluble in titanium oxide. Thus, the oxidized dopant does not form a solid solution with titanium oxide. The amorphous material may be deposited as a coating for small applications by processes such as sputter, evaporation, sol gel, spray, or any other suitable means, and as a coating for large-scale applications by an energetic process, such as sputter, or any other suitable means. Sputtering processes can be any known in the art, such as a process employing rotating cylindrical magnetrons, as described in Lehan et al., U.S. Patent No. 5,814,195, and Wolfe et al., U.S. Patent No. 5,047,131, both of which are expressly incorporated herein in their entireties by this reference, or any other suitable means.

In one embodiment, the dielectric and the additive are deposited energetically in a well-mixed amorphous state. The deposition rate and the substrate temperature ("T") determine whether the film is deposited in an amorphous state. Fig. 3 shows a graph of the deposition rate versus inverse temperature with the vertical axis 43 representing the absolute deposition rate in angstroms / second, and the horizontal axis 41 representing $1/T$ in $1/^\circ\text{C}$. If the film is deposited under the conditions of region 45, then the film will be epitaxial. If the film is deposited under the conditions of region 47, then the film will be polycrystalline. If the film is deposited under the conditions of region 49, then the film will be amorphous. Thus, to achieve an amorphous film, the absolute deposition rate has to be high, and/or the substrate temperature very low. For example, in the reactive deposition of titanium oxide, a deposition rate greater than about five angstroms / second with a substrate temperature in the range of about twenty to about forty degrees Celsius produced an amorphous titanium oxide films. Higher substrate temperatures may require higher deposition rates. The absolute deposition rate, the substrate temperature, and the factors that affect the absolute deposition rate or the substrate temperature vary depending on the type of machine, such as a deposition apparatus, since the conditions at the substrate may vary according to apparatus and affect the surface mobility of the atoms. For example, in a deposition apparatus, the deposition rate is affected by the materials of the film, the power, the mixture of gases, for example, the argon to oxygen ratio, and the pressure.

Once an optical coating has been deposited onto the substrate, such as a transparent substrate like glass or a CRT, the coated substrate is heated to a temperature higher than a heat-treatment temperature of the substrate. For example, coated glass is

heated to its bending temperature of approximately 650°C or higher in order to bend it, or a coated CRT is heated to about 430°C in order to make a frit seal. The glass is then shaped or bent appropriately for its future application in windshields, back and side automobile windows, headlights, architectural glass, or the like.

- 5 The invention is described in more detail by the way of the following example. The following example is presented solely for the purpose of further illustrating and disclosing the present invention, and is not to be construed as limiting the invention.

Example 1

- 10 One example of an a-TiXO compound is Ti-Si-O. Titanium and silicon are insoluble in each other in their oxidized states and form no solid solutions. Ti-Si-O compounds were deposited on glass using a co-sputtering process. One target was coated with titanium, while the other target was coated with silicon. The pressure was 3.25 mtorr. The process plasma consisted of 40 sccm of oxygen and 35 sccm of argon. A 643
15 angstrom film with 0% atomic percent of silicon dioxide and 100% atomic percent of titanium oxide was deposited using a power of 5.0 kW for the titanium target, and three passes of the substrate through the sputtering machine at a pass rate of 6.2 inches / minute. A 742 angstrom film with 13% atomic percent of silicon dioxide and 87%
20 atomic percent of titanium oxide was deposited using a power of 5.0 kW for the titanium target and 0.3 kW for the silicon target, and three passes of the substrate at 6.2 inches / minute. A 906 angstrom film with 27% atomic percent of silicon dioxide and 73%
25 atomic percent of titanium oxide was deposited using a power of 5 kW for the titanium target and 1.0 kW for the silicon target, and one pass of the substrate at 7.4 inches/ minute. For the films with 13% and 27% atomic percent of silicon dioxide, titanium and silicon reacted with oxygen in the plasma to form a Ti-Si-O coating on the glass.

- 30 The amorphous films were examined to determine the crystallization temperature of each amorphous film. An amorphous film has no grain boundaries, while a crystallized film does. Crystallization of the amorphous film can be determined from x-ray diffraction, electron diffraction, imaging, or any other suitable means. In x-ray

diffraction, an amorphous film has dull, very flat peaks in the spectra, which do not correspond to any lattice spacing. As a film becomes more crystalline, more peaks appear, and the peaks grow in intensity. In electron diffraction, the rings sharpen as the film becomes more crystalline. In imaging, the grains grow as the film becomes more crystalline. These different methods for determining the crystallization temperature of a substance are well known in the art.

The specimens were put in a transmission electron microscope ("TEM") with a heating stage. The film with 0% atomic percent of silicon dioxide began nucleation at a temperature of around 300°C, continuing until fully crystallized. Nucleation was evidenced by very small grain size, which indicated the crystallization of the film. There was no growth of grains up to 700°C, but there were many nucleation sites.

The film with 13% atomic percent of silicon dioxide was amorphous at room temperature. There were no signs of nucleation or segregation into grains at temperatures of up to 120°C. At 200°C, small particles began appearing but with a very slow growth so that only a few percentages of the film were in a crystal state. At 550°C, the growth rate increased dramatically with a major portion of the film in the crystalline state.

The film with 27% atomic percent of silicon dioxide was amorphous at room temperature. The crystallization activity of the 27% atomic percent of silicon dioxide film was checked from 150°C to 800°C at 50°C intervals. No crystallization activity was observed until between about 700°C to about 800°C. At 750°C, low density nucleation sites were detected with bright field TEM, which indicated crystallization of the film. Only at 800°C was the film sufficiently crystallized to produce a polycrystalline electron diffraction pattern.

The film with 0% atomic percent of silicon dioxide had a crystallization temperature of about 350°C, which is below the heat-treatment temperature of most substrates. Thus, this film would likely be unsuitable for most substrates undergoing heat treatment. The film with 13% atomic percent of silicon dioxide had a crystallization temperature of about 550°C, and the film with 27% atomic percent of silicon dioxide had a crystallization temperature of about 700°C to about 800°C. The film with 13% atomic percent of silicon dioxide could be used in applications that have a heat-treatment temperature below its crystallization temperature of about 550°C, like fritting, which has a heat-treatment temperature of about 400°C. The film with 27% atomic percent of

silicon dioxide could be used in applications that have a heat-treatment temperature below its crystallization temperature of about 700°C to about 800°C. For example, fritting is performed at about 400°C, heat strengthening at about 600°C, bending at about 650°C, and tempering at about 730°C.

5 The atomic percent of silicon dioxide was approximated from the index of refraction of the film. The index of refraction was measured optically, as is known in the art. The crystallization temperature of the film with 0% atomic percent of silicon dioxide was determined to be about 350°C, and the index of refraction was found to be about 2.45. The crystallization temperature of the film with 13% atomic percent of silicon
10 dioxide was determined to be about 550°C, and the index of refraction was found to be about 2.35. The crystallization temperature of the film with 27% atomic percent of silicon dioxide was determined to be about 700°C to 800°C, and the index of refraction was found to be about 2.2. Figure 4a shows that the crystallization temperature increases with a decrease in the index of refraction for Ti-Si-O. Figure 4b shows that the
15 crystallization temperature increases with an increase in silicon content for Ti-Si-O.

 The amorphous films with 13% and 27% atomic percent of silicon dioxide prepared as in the above example can be used in optical coatings, particularly heat-treatable optical coatings. The additive and its atomic percent in the amorphous film are selected to suit the requirements of crystallization temperature and index of refraction for
20 a particular application. For example, an amorphous film with titanium oxide and 27% atomic percent of silicon dioxide survived the heat treatment of a substrate coated with the amorphous film to the bending temperature around 650°C or above. Alternatively, the additive, crystallization temperature, or index of refraction can be selected for a particular application.

25 An advantage of this invention is the ability of a high refractive index, amorphous material to survive heat-treatment of a substrate, such as glass. Thus, a substrate can be coated with the heat-treatable amorphous material and subsequently heated without destroying the film. In addition, the amorphous material reduces the oxidation of underlying layers, such as metallic layers, at high temperatures, which would otherwise
30 cause the optical properties of the stack to change after heat treatment. The amorphous material may also reduce or prevent diffusion of contaminants between layers. Thus, the amorphous material is advantageously used in an optical coating, such as an anti-

Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100
1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100	

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